

Impact of redox conditions on thermal deactivation of NO_x traps for diesel

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Abstract

Performance of NO_x traps after high-temperature treatments in different redox environments was studied. Two types of treatments were considered: aging and pretreatment. Lean and rich agings were examined for a model NO_x trap, Pt–Ba/Al₂O₃. These were done at 950 °C for 3 h, in air and in 1% H₂/N₂, respectively. Lean aging had a severe impact on NO_x trap performance, including HC and CO oxidation, and NH₃ and N₂O formation. Rich aging had minimal impact on performance, compared to fresh/degreased performance. Deactivation from lean aging was essentially irreversible due to Pt sintering, but Pt remained dispersed with the rich aging. Pretreatments were examined for a commercially feasible fully formulated NO_x trap and two model NO_x traps, Pt–Ba/Al₂O₃ and Pt–Ba–Ce/Al₂O₃. Pretreatments were done at 600 °C for 10 min, and used feed gas that simulated diesel exhaust under several conditions. Lean pretreatment severely suppressed NO_x, HC, CO, NH₃ and N₂O activities for the ceria-containing NO_x traps, but had no impact on Pt–Ba/Al₂O₃. Subsequently, a relatively mild rich pretreatment reversed this deactivation, which appears to be due to a form of Pt–ceria interaction, an effect that is well known from early work on three-way catalysts. Practical applications of results of this work are discussed with respect to NO_x traps for light-duty diesel vehicles.

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1. Introduction

Diesel and lean-burn gasoline engines are considered attractive alternatives to conventional gasoline to improve fuel economy and reduce CO₂ emissions for light duty vehicles. A major challenge is abatement of NO_x (NO + NO₂) emissions. This is difficult in the O₂-rich exhaust of lean-burn engines. Lean NO_x traps have been an important aftertreatment technology under development to address this [1–3]. Recently, NO_x traps have been produced for lean burn gasoline passenger cars, but this application is limited. A key obstacle in the way of more widespread implementation of NO_x traps is durability. This is particularly the case for diesel vehicles. They require high NO_x conversion at lower temperature than that needed for

lean-burn gasoline, for example, ~150–300 °C for diesel compared to ~300–600 °C for gasoline. NO_x trap activity at the lower temperatures is particularly sensitive to catalyst deactivation.

One source of deactivation is sulfur [4,5]. Vehicle exhaust contains low levels (ppm) of SO₂. This is derived primarily from combustion of organic sulfur contaminants in fuel. Sulfates accumulate on NO_x storage sites, and degrade performance. Periodically, sulfate is purged from the trap to restore NO_x performance. Sulfate purging (deSO_x) as well as the more frequent NO_x purging (deNO_x) is accomplished by running the engine rich, however, much higher temperatures are needed for deSO_x. For example, ~600–750 °C is typical for deSO_x, where normal operating temperatures are sufficient for deNO_x. In addition, a deSO_x event requires longer time, 5–10 min, compared to a few seconds for a deNO_x event.

Another source of deactivation is thermal, which is the subject of this work. In particular, we examined effects of feed gas redox character during high temperature on NO_x trap

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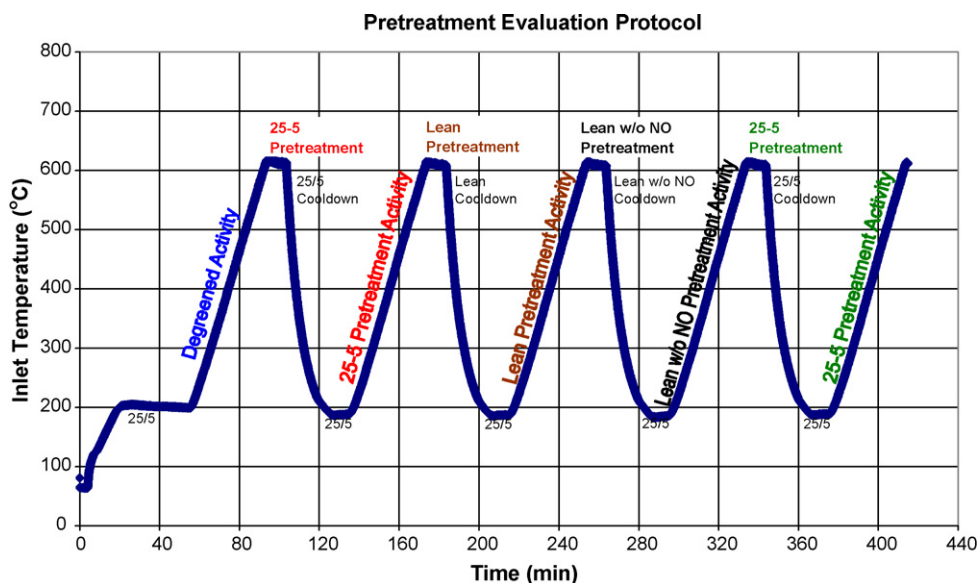


Fig. 1. Pretreatment evaluation procedure.

performance. We evaluated effects of aging, as well as shorter-term high-temperature exposure. In diesel applications, NO_x traps require high temperature for sulfate purging, as described above, and for regeneration of a downstream soot filter. The former requires a reducing (rich) environment, and the latter an oxidizing (lean) environment. Practical implications of this work are discussed.

2. Experimental

2.1. NO_x trap samples

Two model NO_x traps and one fully formulated NO_x trap, all prepared by a commercial catalyst supplier, were examined. Both model traps contained Pt and BaCO_3 supported on $\gamma\text{-Al}_2\text{O}_3$. One also contained ceria (CeO_2). These two model traps will be referred to as Pt–Ba/ Al_2O_3 and Pt–Ba–Ce/ Al_2O_3 . The fully formulated trap contained Pt, BaCO_3 and ceria on $\gamma\text{-Al}_2\text{O}_3$, however, its entire composition is proprietary. This trap will be referred to as supplier formulated, or simply supplier. All NO_x traps were provided as washcoated cordierite monoliths with 400 cells/in.². Their Pt loadings were ~ 100 g/ft³.

Table 1
Simulated diesel exhaust gas composition used for NO_x trap activity evaluations

Feed gas components	Lean concentrations	Rich concentrations
NO_x	500 ppm	500 ppm
C_3H_6	100 ppm	1650 ppm
CO	500 ppm	4.0%
H_2	167 ppm	1.3%
O_2	10%	1%
CO_2	5%	5%
H_2O	5%	5%
N_2	Balance	Balance

2.2. Activity testing

An integral flow reactor was used to measure NO_x trap activity. NO_x trap test samples were (3/4) in. diameter \times 3 in. long monolith cores cut from larger sample bricks. The reactor had a quartz flow tube in which a test sample was placed. Thermocouples were located in the feed gas ((3/4) in. before the sample inlet) and in the sample (1 in. behind the inlet face). Temperature was controlled primarily with a large tube furnace (29 in. long) that surrounded the flow tube. The sample zone was isothermal with $\Delta T < 10$ °C at 600 °C. The flow tube had a bypass line to allow measurement of inlet concentrations for the feed gas components. Feed gas was a simulated diesel exhaust gas mixture. Typical diesel exhaust is lean (O_2 -rich), however, NO_x traps periodically require rich exhaust to release and reduce stored NO_x . Compositions for the lean and rich feed gas mixtures are described in Table 1.

Activity data were collected over a temperature range of 150–600 °C, measured at the sample inlet. Temperature was ramped at 10 °C/min. Space velocity was 30,000/h. Feed gas composition was cycled between lean and rich, 25 and 5 s, respectively, which is called 25–5. FTIR was used to measure NO , NO_2 , NH_3 , N_2O , C_3H_6 , and CO concentrations. Its pathlength was 3.25 m. Resolution was 0.5 cm^{−1}. The FTIR gas cell was ~ 150 cm³ in volume, and gas flow was ~ 3 l/min. Measurement frequency was ~ 1 Hz. Conversions for NO_x , HC and CO were calculated as $[(C_{\text{inlet}} - C_{\text{outlet}})/C_{\text{inlet}}] \times 100\%$, where C is concentration averaged over one 25–5 cycle. Formation for NH_3 and N_2O were calculated as $[C_{\text{outlet}}^{\text{NH}_3}/C_{\text{inlet}}^{\text{NO}_x}] \times 100\%$ and $[2C_{\text{outlet}}^{\text{N}_2\text{O}}/C_{\text{inlet}}^{\text{NO}_x}] \times 100\%$, respectively.

Degreening was performed on all samples, fresh and aged, prior to activity testing. Samples were degreened in the flow reactor by holding inlet temperature at 600 °C for 0.5–1 h. Feed gas was cycled at 25–5, which was also performed during heating and cooling.

2.3. Aging

Lean and rich agings were performed on Pt–Ba/Al₂O₃ samples. Monolith pieces were aged in a tube furnace at 950 °C for 3 h. Lean aging was carried out in air, and rich aging was carried out in flowing N₂ with 1% H₂.

2.4. Pretreatment

The effect of pretreatment on NO_x trap performance was evaluated using the protocol depicted in Fig. 1. Test samples were degreened prior to subjecting to this procedure. The protocol started with stabilizing inlet temperature at ~150–200 °C. Feed gas was cycled at 25–5. When outlet gas concentrations became stable, temperature was ramped to 600 °C at 10 °C/min. Activities were measured during this and the four subsequent temperature ramp-ups shown in Fig. 1. After each activity ramp, inlet temperature was held at 600 °C for 10 min. During this period, pretreatment was performed for the next activity ramp. Four pretreatments were examined in sequence, as shown in Fig. 1. They were carried out with the following feed gas compositions: (1) 25–5; (2) lean; (3) lean w/ o NO; and (4) repeat 25–5. Pretreatment feed gas continued during the cool-down. When the inlet temperature reached ~150–200 °C, it was held constant for 10 min to stabilize NO_x trap conditions before the next activity ramp. Feed gas was cycled at 25–5 during this time. There were five activity ramps in this procedure: an initial degreened activity and the four pretreated activities. The degreened activity and the first 25–5 activities were comparable, so the former was not included in the results presented below.

2.5. Chemical–physical analysis

X-ray diffraction (XRD) patterns were obtained with a Scintag X2 diffractometer using Cu K α radiation. Washcoat material removed from a monolith was analyzed. This

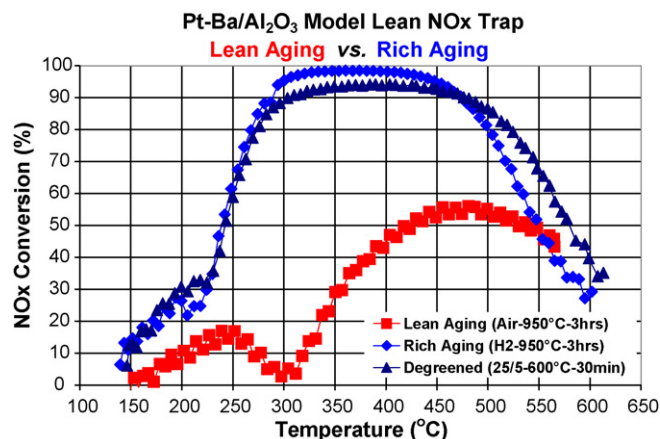


Fig. 2. NO_x conversion over Pt–Ba/Al₂O₃ after (a) lean aging, (b) rich aging, and (c) degreening.

washcoat material was packed loosely in a shallow cavity, 0.5 mm deep and 9 mm in diameter, which had been cut into a “zero-background” quartz sample holder.

3. Results and discussion

3.1. Lean vs. rich aging

Fig. 2 compares NO_x conversion vs. inlet temperature for a lean aged, a rich aged, and a degreened Pt–Ba/Al₂O₃ catalyst. The lean aging caused severe decrease in NO_x performance, whereas the rich aging showed performance similar to that of the degreened sample. Both agings were performed at the same temperature and time, 950 °C for 3 h. Lean aging was carried out with air, and rich aging was carried out with 1% H₂/N₂. Pretreatment before performance measurements was 25–5 at 600 °C for 10 min.

For other feed gas species, activity degradation after lean and rich aging was analogous to the NO_x results. That is, the lean aging severely deteriorated HC and CO performance, shown in

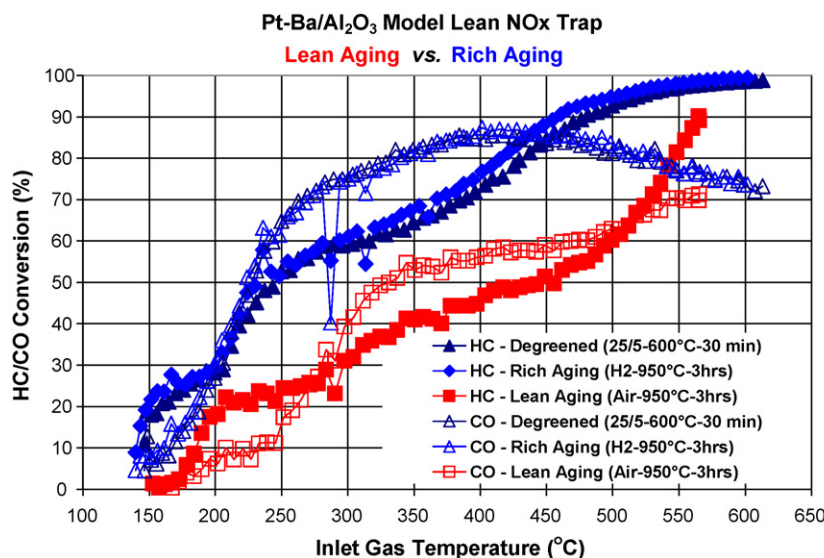


Fig. 3. HC and CO conversions over Pt–Ba/Al₂O₃ after (a) degreening, (b) rich aging, and (c) lean aging.

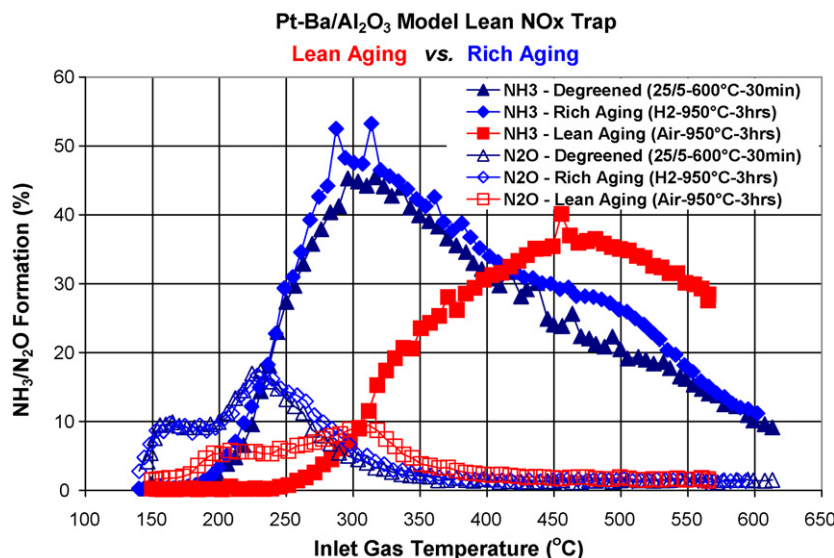


Fig. 4. NH_3 and N_2O formation over Pt-Ba/ Al_2O_3 after (a) degreening, (b) rich aging, and (c) lean aging.

Fig. 3, whereas the rich aging had minimal impact. NH_3 and N_2O formation in Fig. 4 are similar for the rich aged and degreened samples. For the lean aged sample, NH_3 formation peaks at a higher temperature, and a larger portion of the converted NO_x becomes NH_3 ($\sim 2/3$ of the converted NO_x in Fig. 2).

The features in the HC and CO conversion profiles in Fig. 3 merit some discussion. One should keep in mind that each point in these curves is an average conversion over each cycle of 25 s lean/5 s rich. For HC, light-off initially quenches at $\sim 25\%$ conversion. Inspection of the time-resolved raw data shows HC initially consumed almost exclusively during the lean pulses. These contain $\sim 25\%$ of total HC over a cycle which points to the source of the initial light-off feature. Features above 25% conversion are due to HC reactions during rich pulses (e.g., oxidation by NO and O_2 , and steam reforming), however, characterizing these features further is beyond the scope of this work. For CO, conversion fall off above $\sim 400^\circ\text{C}$ is consistent

with thermodynamics of water-gas shift, but further work would be needed to confirm. It may be noted below that these features do not show up in data for the supplier formulated NO_x trap, and this is probably due to higher activity.

X-ray diffraction patterns for the lean aged, rich aged, and untreated samples are shown in Fig. 5. These data reveal sintered Pt after the lean aging, as has been seen previously [6]. Solid circles mark the position of Pt diffraction peaks, none of which are seen for the rich aged and untreated samples. Appearance of Pt peaks in the lean aged sample is due to coarsening, or sintering, of Pt that was initially well dispersed. Average Pt particle size of ~ 50 nm was estimated from the inverse of peak width. After rich aging, Pt remains dispersed as indicated in our previous work [6] that used a similar aging treatment. Pt sintering is dramatically faster under oxidizing conditions because Pt can move and redistribute via vapor phase transport of volatile Pt oxides [7]. Under reducing

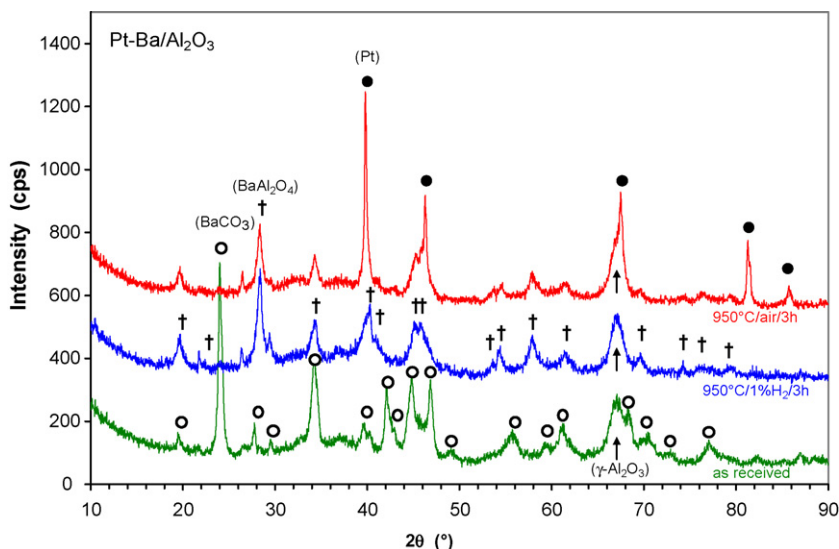


Fig. 5. XRD patterns for Pt-Ba/ Al_2O_3 : (a) as-received, (b) aged at 950°C in 1% H_2 in N_2 for 3 h, and (c) aged at 950°C in air for 3 h.

conditions, the mechanism is surface movement of Pt^0 atoms/clusters, which is a much slower process [7,8].

Pt dispersion is linked to HC, CO, NH_3 and N_2O activities, however, both Pt and Ba dispersion should contribute to the NO_x performance. The similar activities for the rich aged and degreened samples are consistent with Pt remaining dispersed after rich aging. However, after lean aging, the suppressed activities indicate significant modification of Pt. XRD revealed sintered Pt. It was not only less active for NO_x , HC and CO performance, but also more selective for converting NO_x to NH_3 rather than N_2 .

Ba species were also identified in the diffraction patterns in Fig. 5. Peaks from BaCO_3 (marked by open circles) were found for the untreated sample, and BaAl_2O_4 peaks (marked by daggers) were found for both of the aged samples. The latter is produced by reaction of BaCO_3 and $\gamma\text{-Al}_2\text{O}_3$ at temperatures above 600°C [9,10]. The similarity in performance observed for the untreated and rich aged samples suggests that storage of NO_x does not depend strongly on the initial form of the trapping material, i.e., both BaCO_3 and BaAl_2O_4 are effective [10]. Surface area of Ba^{2+} components and their contact with Pt appear to be major factors that impact storage capacity of the trap [9,11].

3.2. Effect of lean pretreatment

3.2.1. Supplier formulated NO_x trap

Fig. 6 shows the effect of pretreatment on NO_x conversion for a degreened supplier formulated NO_x trap sample. The four NO_x performance curves were acquired in sequence after the following pretreatments, as shown in Fig. 1: (1) lean-rich cycle (25–5 s); (2) lean; (3) lean w/o NO ; (4) lean-rich cycle. The first pretreatment was considered the reference condition, and repeated for the fourth curve. Both are labeled 25–5 in the figure legend with the repeat listed last. Each pretreatment was performed at 600°C for 10 min.

These data show lean pretreatment caused severe, but reversible deactivation for the supplier NO_x trap at temperatures

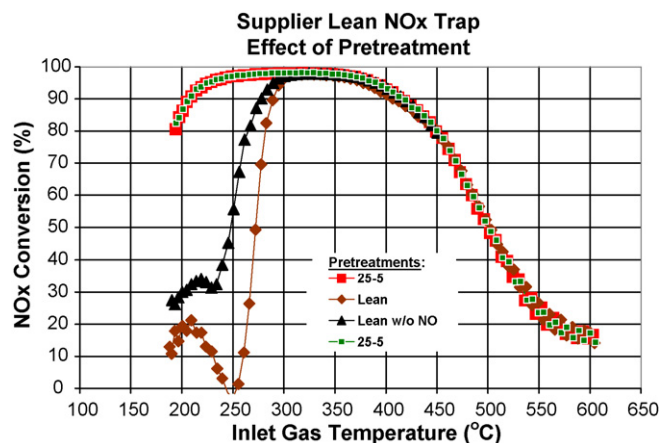


Fig. 6. Effect of pretreatment on NO_x performance for supplier NO_x trap.

below 300°C . Deactivation was somewhat less with NO removed during lean pretreatment, possibly related to less NO_x stored initially. Original activity was completely restored when the trap was subjected to the reference pretreatment of 25–5 cycling for the fourth curve. Rich pretreatment was examined in a separate experiment, and did not alter activity. These results indicate that there were transient changes in the trap surface chemistry due to the lean pretreatments, and that O_2 and NO_x each influenced the changes, with the former having primary impact.

Reversible effect of lean pretreatment on HC and CO oxidation and on NH_3 and N_2O formation are shown in Figs. 7 and 8, respectively. HC and CO oxidation showed similar reversible deactivation as NO_x conversions in Fig. 6. NH_3 and N_2O formation shifted to higher temperatures after the lean pretreatments, and went back after 25–5 pretreatment.

3.2.2. Model NO_x traps

Effect of pretreatment examined for model NO_x traps provided insight into changes in the surface chemistry

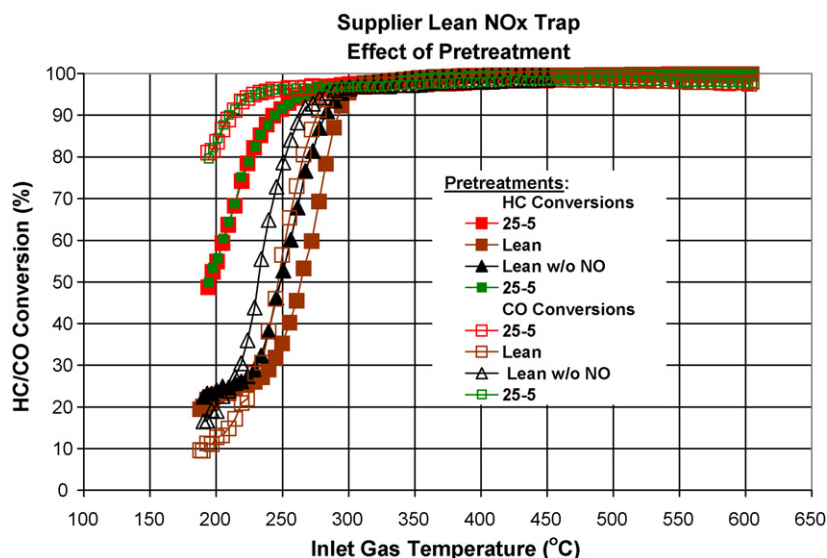


Fig. 7. Effect of pretreatment on HC and CO conversion for supplier NO_x trap.

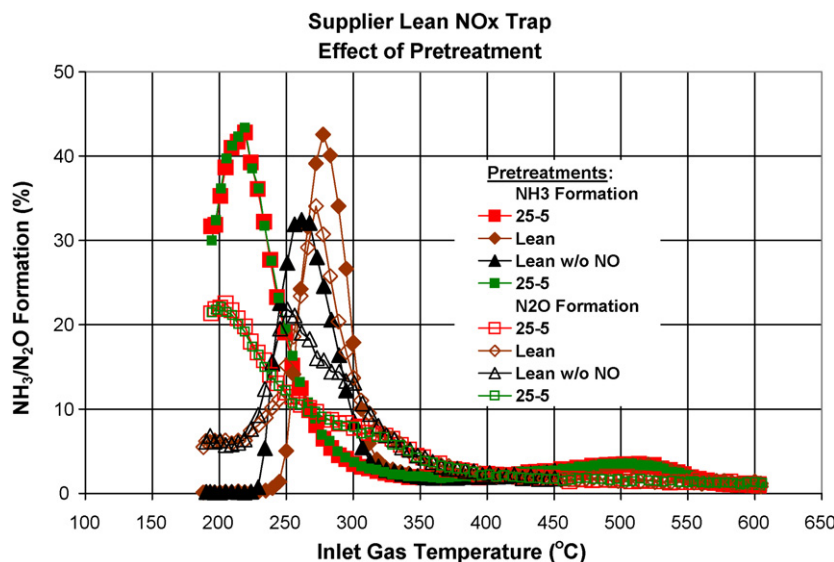


Fig. 8. Effect of pretreatment on NH₃ and N₂O formation for supplier NO_x trap.

responsible for the reversible deactivation of the supplier NO_x trap. Two model systems were studied: Pt–Ba/γ-Al₂O₃ and Pt–Ba–Ce/γ-Al₂O₃. (The supplier NO_x trap above also contained Pt, Ba, and Ce.)

NO_x performance for Pt–Ba/γ-Al₂O₃ in Fig. 9 did not show deactivation from lean pretreatment displayed by the supplier NO_x trap (Fig. 6). There was no impact on NO_x conversion for the lean pretreatment that included NO. This was also the case for HC and CO oxidation in Fig. 10, and for NH₃ and N₂O formation in Fig. 11. When the lean pretreatment had NO removed, the trap was depleted of stored NO_x. This caused enhanced NO_x conversions for temperatures below 250 °C, and lowered peak N₂O formation. HC and CO performance was unaffected.

When ceria (CeO₂) was added to the Pt–Ba model system (Pt–Ba–Ce/γ-Al₂O₃), Figs. 12–14 show lean pretreatment suppressed activities similar to that observed for the supplier formulation (Figs. 6–8). Performance recovered, although only partially, after the standard pretreatment of 25–5 lean-rich cycling. (A possible reason for only partial recovery, as

opposed to full recovery that was seen for the supplier catalyst, is advanced later.)

Results for the model traps thus suggest that ceria is involved in the reversible deactivation of the supplier formulated NO_x trap. We propose that this deactivation is simply a consequence of a well-known metal–support interaction, wherein ceria serves as a promoter of Pt in performing the three-way catalytic reactions needed to regenerate the NO_x trap during the rich portion of the lean-rich cycle. A condition for such promotion is that the noble metal be in contact with ceria, which necessarily leads to the possibility of unwanted interaction, as well. It has been shown previously that ceria-supported Pt and Rh catalysts undergo deactivation following an oxidation treatment (at 600–900 °C), but recover their initial activities following a reduction treatment (at 300–450 °C), where CO and HC oxidation reactions were used to characterize catalyst activity [12,13]. Shifts in light-off between the two pretreatments were typically of order 100 °C, similar to those found in this study. (Pd catalysts did not display this behavior, however.)

Although structural characterization of this phenomenon goes beyond the scope of the present study, a brief description of the fundamental processes generally believed to underlie the interaction between Pt and ceria provides for a more complete discussion of this effect. The basic mechanism of the unwanted Pt–CeO₂ interaction can thus be described as ceria-facilitating changes in the oxidation state of Pt. Ceria is a well-known oxygen storage component because of the ability of Ce to rapidly change oxidation state, i.e., Ce^{IV} ↔ Ce^{III}. This occurs in response to changes in redox conditions of its feed gas environment. Removal and addition of oxygen accompanies the reversible oxidation state, i.e., 2Ce^{IV}O₂ ↔ Ce^{III}₂O₃ + (1/2)O₂. Pt lowers the activation barrier for this reaction. Evidence for this is lower reduction temperature of ceria and increased oxygen storage capacity when Pt is present [14]. In turn, the reversible deactivation, described above, is evidence that ceria lowers the activation barrier for Pt oxidation. (Pt⁰ is presumed to be more catalytically active than the Pt^{II/IV} species.) It has been suggested

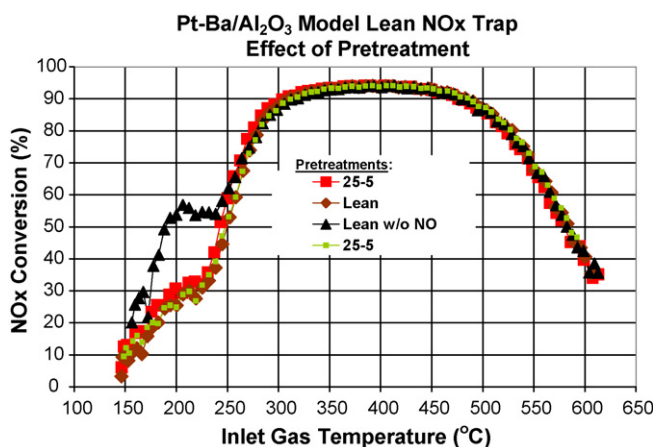
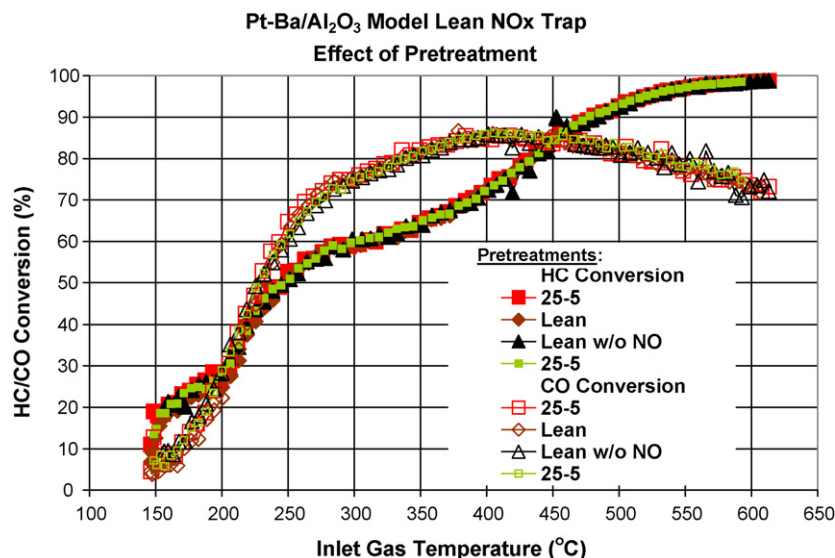
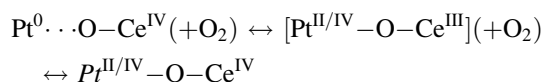


Fig. 9. Effect of pretreatment on NO_x performance for Pt–Ba/Al₂O₃.

Fig. 10. Effect of pretreatment on HC and CO conversion for Pt-Ba/Al₂O₃.

that Ce can draw charge from Pt [12]. This makes it easier to oxidize and reduce Pt ($\text{Pt}^0 \leftrightarrow \text{Pt}^{\text{II/IV}}$), for example, under the temperature–time conditions of the pretreatments. Transfer of electrons between Ce and Pt requires that they be coupled. This likely occurs through an O-bridge bond:



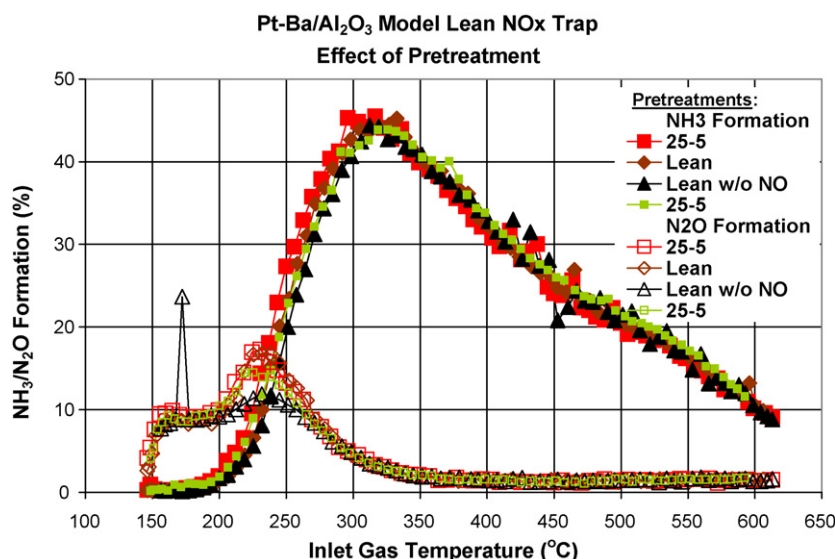
The deactivated $\text{Pt}^{\text{II/IV}}$ species is thus believed to be an O-coupled Pt–Ce species. Support for such a Pt–O–Ce species can be found in a review article [15].

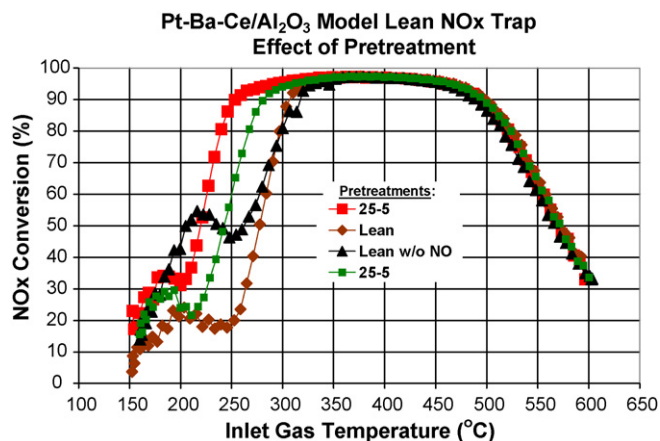
Note that the Pt–CeO₂ interaction described above and in reference [13] differs from the so-called strong metal–support interaction (SMSI). The SMSI terminology was originally proposed to describe various effects of redox treatments on Pt/

TiO₂. Therein reductive treatment at high temperature leads to deactivation of the catalyst through either metal decoration by sub-oxides from the support or electronic interaction, and oxidative treatment restores the catalyst activity by reversing these effects. Such SMSI has, indeed, been well documented for noble metals (Pt, Pd, Rh) supported on ceria, ceria–zirconia, etc. [16]. In our situation, however, the oxidative treatment causes deactivation, whereas the reductive treatment restores activity, i.e., just the opposite of SMSI behavior. Another example of a metal–support interaction similar to the one invoked here occurs for Rh supported on alumina [17], where it is generally believed that some form of Rh–O–Al species, derived from oxidized rhodium and alumina, is involved.

3.2.3. Relative performance of different NO_x traps

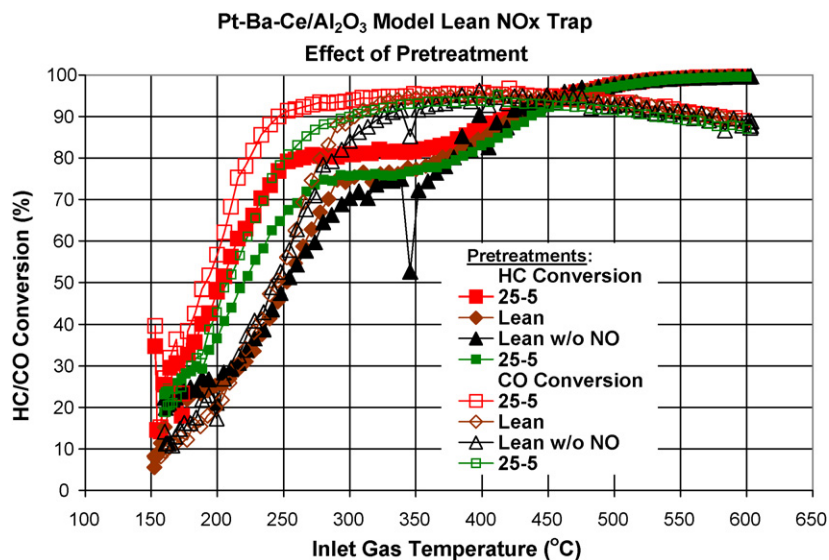
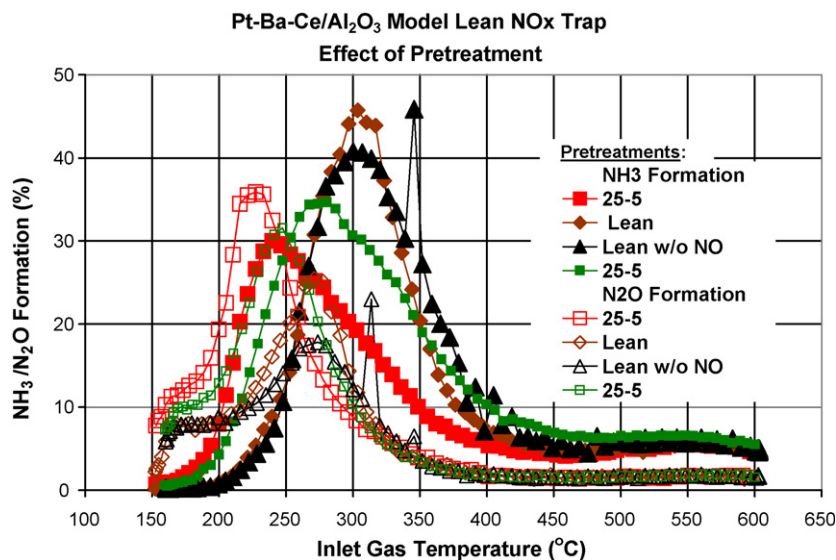
In comparing NO_x performance for the supplier trap, Pt–Ba/γ-Al₂O₃, and Pt–Ba–Ce/γ-Al₂O₃ (Figs. 6, 9 and 12,

Fig. 11. Effect of pretreatment on NH₃ and N₂O formation for Pt–Ba/Al₂O₃.

Fig. 12. Effect of pretreatment on NO_x performance for Pt–Ba–Ce/Al₂O₃.

respectively), the Pt–Ba model trap was the least active over the low temperatures: Pt–Ba < Pt–Ba–Ce < supplier, where all had similar Pt loadings. However, Pt–Ba was more active at low temperatures than the other two NO_x traps after lean pretreatment, consistent with the metal–support interaction effect discussed above. In addition, Pt–Ba had a much wider temperature window for NH₃ formation, extending to 500 °C (for 20% NH₃ formation), compared to 300 °C for Pt–Ba–Ce, and 250 °C for the supplier NO_x trap.

It is worth pointing out that the higher NO_x performance at low temperatures for Pt–Ba–Ce compared to Pt–Ba appears to have minimal contribution from an increase in bed temperature, which is often associated with ceria. Bed temperature was measured 1 in. from the inlet of a 3 in. long sample. During light-off, 30 s-averaged bed temperature was ~25 °C higher than the inlet temperature at 50% conversion for both NO_x traps. This is shown in Fig. 15 where NO_x conversion was

Fig. 13. Effect of pretreatment on HC and CO conversion for Pt–Ba–Ce/Al₂O₃.Fig. 14. Effect of pretreatment on NH₃ and N₂O formation for Pt–Ba–Ce/Al₂O₃.

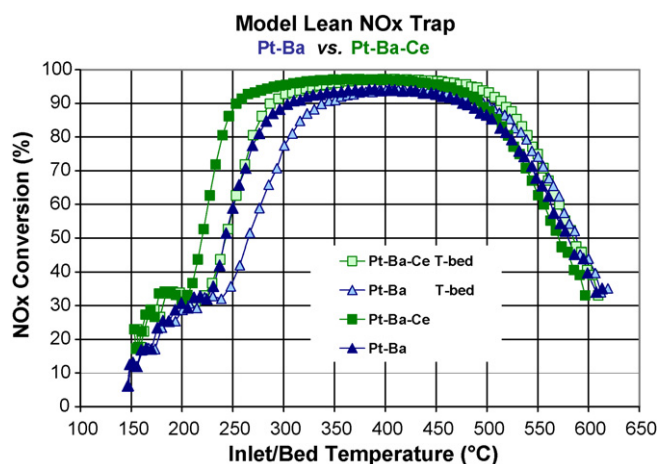


Fig. 15. NO_x conversions plotted against bed temperature and inlet temperature for Pt–Ba/ Al_2O_3 and Pt–Ba–Ce/ Al_2O_3 .

plotted against bed temperature and inlet temperature. Also, variation in bed temperature during the 25–5 evaluation cycling was similar for both traps.

The width of the temperature window for NH_3 formation appears to be correlated with that of incomplete HC oxidation. In particular, Pt–Ba and Pt–Ba–Ce data for HC oxidation show a temperature window of relatively constant, but incomplete, HC conversion (Figs. 10 and 13, respectively), starting at the temperature where NH_3 formation peaks (Figs. 11 and 14), extending through the high-temperature side of the NH_3 formation window. In the supplier trap, NH_3 is only formed during HC light-off; at higher temperatures, where HC oxidation is complete, no NH_3 is observed (Figs. 7 and 8).

Effect of pretreatment on peak levels for NH_3 and N_2O formation was compared for the different NO_x traps (Figs. 8, 11 and 14). The supplier and Pt–Ba–Ce NO_x traps produced lower peak NH_3 and N_2O levels for lean w/o NO pretreatment than for lean. Pt–Ba also produce lower peak N_2O for lean w/o NO, however, peak NH_3 was unaffected. Lower peak levels for NH_3 and N_2O may be related to lower NO_x storage levels produced when NO was absent during pretreatment. Although the supplier and Pt–Ba–Ce traps displayed similar reversible deactivation, as described above, peak levels for NH_3 relative to N_2O often differed. For example, the 25–5 pretreatment produced higher peak NH_3 level than N_2O for the supplier trap, but peak NH_3 and N_2O levels were roughly the same for Pt–Ba–Ce. This difference is likely due to other components or characteristics in the proprietary supplier formulation.

Along the same lines, we speculate that the incomplete restoration of initial performance of Pt–Ba–Ce relative to supplier trap during pretreatment testing reflects a significant difference in ceria incorporation between the two: possible use of stabilized high-surface-area ceria in the supplier trap [17]. In the model trap, a pretreatment temperature of as little as 600 °C could well have stimulated partial separation of Pt and ceria (via coarsening of ceria), leading to partial loss of both the promotional effect of ceria and the unwanted, deactivating interaction. In the supplier trap, on the other hand, much better metal–ceria contact would have been maintained.

3.3. Practical implications for minimizing deactivation

3.3.1. Applications

This work revealed that high-temperature oxidizing conditions diminished NO_x trap activity, in most cases, where reducing conditions did not. On diesel vehicles, NO_x traps will be subjected to periods of high temperature (~ 5 – 10 min at $T > 550$ °C), such as desulfation and filter regeneration. Although the former requires rich feed gas, lean excursions are used in engine desulfation procedures to stabilize and prevent run away temperature. Cumulative effect of lean high-temperature periods produce aging, which we examined. Also, our pretreatment study revealed an individual lean high-temperature event produced reversible deactivation when NO_x trap contained ceria.

3.3.2. Suggestions concerning aging

On diesel engines, stabilizing a high temperature for deSO_x , while exhaust is rich, is difficult. High temperature is usually generated from exotherm of HC/CO oxidation on the NO_x trap, or an upstream catalyst. In rich exhaust, since there is excess HC/CO, the O_2 level dictates the magnitude of exotherm. Typical rich O_2 levels of 1–2% cause runaway temperature, easily exceeding 850 °C. To avoid this, the engine is switched lean, which drops HC/CO to ppm levels essentially quenching the exotherm. Ideally, the challenge is to produce rich diesel exhaust with sufficiently low O_2 levels to stabilize an appropriate deSO_x temperature (~ 600 – 750 °C). However, there is a concern with this strategy. It is unclear whether O_2 in rich, high-temperature conditions yields highly volatile PtO_2 that leads to Pt sintering. This would depend on the rate of reductant consumption of O adsorbed or bonded to Pt vs. that for volatilization of Pt oxides, specifically comparing in a rich environment. Future experiments could be designed to address this.

If continuous rich desulfation is viable on a diesel, one might consider simultaneously regenerating a downstream soot filter by injecting air in front of it. This strategy could improve NO_x trap durability because its high-temperature environment is rich during filter regeneration. However, since filter regeneration is needed more often than desulfation, perhaps three to four times, this strategy would negatively impact fuel economy if all the filter regenerations were done this way. Model calculations could optimize the strategy.

An alternate approach to improve NO_x trap durability is to develop a more robust formulation. Although it is not possible to entirely dispense with Pt – it is best among precious metals for low temperature NO oxidation activity [18–20], and Pt has better sulfur poisoning resistance over base metal oxides that are active for NO oxidation [20–22] – components can be added to help keep Pt dispersed. One possibility is to alloy Pt with Pd to slow down Pt sintering [23,24] and improve durability, although activity may be compromised [21].

3.3.3. Suggestions concerning reversible deactivation

A lean high-temperature event, such as regeneration of a downstream soot filter, is expected to result in reversible

deactivation for NO_x traps containing ceria. Elimination of ceria to solve this issue is not desirable since ceria provides improved low-temperature performance, as shown by comparing Figs. 9 and 12. In particular, ceria provides oxygen storage capacity, and it also promotes water-gas shift and steam reforming reactions which produce H₂, a more effective reducing agent than CO or HC for NO_x traps [25,26]. According to our pretreatment study, a single filter regeneration will cause substantial deactivation unless, or until, exhaust feed gas is cycled rich during cooling at any temperature above 300 °C [27]. This finding is essentially a generalized operating strategy to avoid this “temporary” deactivation.

Alternatively, a formulation change is another approach to avoid the reversible deactivation. This study implicated an unwanted Pt–CeO₂ interaction as the source of the deactivation. Since Pd–CeO₂ does not display the deactivation–reactivation effect that Pt–CeO₂ and Rh–CeO₂ have shown [12,13], partial substitution of Pd for Pt could be considered (some Pt is needed for NO oxidation, however).

4. Conclusions

Lean aging had a severe impact on NO_x trap performance, whereas rich aging did not. HC and CO performance also degraded, and NH₃ and N₂O formation were affected. Deactivation was essentially irreversible due to Pt sintering. This happens much more rapidly in the air aging, than the 1% H₂/N₂ aging that was done. Pt redistributes via vapor phase transport of volatile Pt oxides, in the former, and via surface transport of Pt⁰ atoms/clusters, in the latter [6,7].

Lean pretreatment had a severe, but reversible impact on activity for ceria-containing NO_x traps. NO_x performance, HC and CO oxidations, and NH₃ and N₂O formations, all shifted to higher temperature. Activities could be recovered by brief rich exposure above 300 °C. The source of this reversible deactivation is believed to be the interaction of Pt and ceria. The latter can rapidly oxidize and reduce, and when coupled with Pt, facilitates changes in Pt oxidation state, where Pt^{II/IV} is presumed to be less active than Pt⁰.

In practice, the aging results apply to long-term durability, and the pretreatment results apply to single events such as regeneration of a downstream soot filter and desulfation of the NO_x trap. Ways to minimize the different types of deactivation were suggested. Both operation and formulation approaches were considered.

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